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PARTICULATE MATTER AND POLYCYCLIC AROMATIC HYDROCARBON DETERMINATION USING A WELL-STIRRED REACTOR (POSTPRINT)

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14. ABSTRACT

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PARTICULATE MATTER AND POLYCYCLIC AROMATIC HYDROCARBON DETERMINATION USING A WELL-STIRRED REACTOR

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ABSTRACT

Combustion generated particulates from gas turbine combustors can cause adverse effects on engine maintenance costs, plume visibility and the environment. Research is being conducted to provide understanding of the mechanisms of soot formation and identify mitigation strategies. A cooled well-stirred reactor (WSR), which simulates the primary zone of a gas turbine combustor, is used in the current study. Experiments have been completed with premixed, fuel-rich ($1.9 < \phi < 2.6$) ethylene-air and ethylene-ethanol-air mixtures. Multiple physical characteristics, including particle number density, particle size distribution, total carbon mass, and (polycyclic aromatic hydrocarbon) PAH content, were used to quantify the soot. A unique instrument, the Particulate Matter Characterization and Monitoring System (PMCMS), was used for the determination of the particle size distribution, and the chemical characterization of the soot and gaseous emissions. The results of the study showed that the benzene concentration in the gas phase increased monotonically with equivalence ratio while the pyrene was shown to correlate with the soot content. The results suggest that pyrene and other PAH species can be used to predict the soot formation for more complex combustion systems. For the conditions of the present study, the addition of ethanol to ethylene was shown to lower soot production compared to pure ethylene.

NOMENCLATURE

CNC	= condensation nuclei counter
GC/MS	= gas chromatograph/mass spectrometer
ICP-MS	= inductively coupled plasma mass spectrometer
RDMA	= radial differential mobility analyzer
m_a	= air mass flow rate (kg/s)
m_f	= fuel mass flow rate (kg/s)
MSVI	= multi-stage virtual impactor
PAH	= polycyclic aromatic hydrocarbon
PFR	= plug flow reactor
PM	= particulate matter
PMCMS	= Particulate Matter Characterization and Monitoring System
R_s	= reflectance of the stained filter
R_w	= reflectance of the unstained filter
SN	= smoke number
T_a	= adiabatic flame temperature (K)
T_f	= reactor temperature (K)
T_o	= inlet temperature (K)
THC	= total hydrocarbons
UNICORN	= UNsteady Ignition and COmbustion with ReactioNs
V	= reactor volume (mL)
WSR	= well-stirred reactor

Symbols

ϕ	= equivalence ratio
ρ	= density (kg/m^3)
τ	= residence time (ms)

INTRODUCTION

The accepted process of soot formation (Figure 1) demonstrates the reaction path to soot by which a portion of fuel is broken into unsaturated radicals and intermediates during combustion. These are known as soot precursors, which then react to form small polycyclic aromatic hydrocarbons (PAH). The growth of PAH continues through further reactions and by collisions and nucleation with each other forming larger PAH, becoming incipient soot particles. These particles continue to grow by processes of surface growth, condensation and coalescence, and through reactions with acetylene and smaller PAH, forming particulate matter (PM) < 50 nm in aerodynamic diameter, referred to as primary soot particles. Primary particles collide and coagulate forming PM ranging in size from hundreds of nanometers to microns. Oxidation continues throughout the combustion process, concurrently and within all stages of PM formation, consuming PAH, the growth species and soot particles comprising PM. Oxidation reactions occur by highly reactive radical species containing OH and oxygen atoms, forming primary combustion products, CO_2, H_2O, CO, NOx, unburned total hydrocarbons (THC) and smoke, an aerosol containing soot.
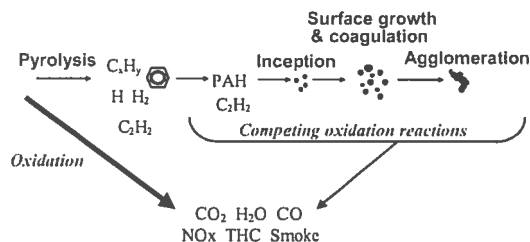

Figure 1: PM Formation Process

To investigate the reduction of PAH and PM due to oxygenates, ethylene fuel (C_2H_4) and ethanol (C_2H_5OH), as an additive, were burned in the Air Force Research Laboratory's Well-Stirred Reactor (WSR)[1-3], while samples were collected from the effluent and analyzed using the Particulate Matter Characterization and Monitoring System (PMCMS)[4]. This study was particularly well-suited for the WSR, which simulates the combustion process in the primary zone of a gas turbine combustor, while eliminating the effects of fuel atomization, evaporation, and mixing processes, and continues the work that was presented in Stouffer et al.[5].

The determination of the PAH and PM generated by the WSR is significant because fundamental information can be evaluated using the PMCMS, before particle inception occurs and after primary particle coagulation into PM. The PMCMS analyses were compared with a predictive model of PAH using UNsteady Ignition and COmbustion using ReactioNs (UNICORN)[6] code which provides quantification and identification of single and multi- ring aromatic hydrocarbons generated in a perfectly stirred reactor.

PM quantification is compared to analyses determined from captured soot and smoke stains, providing further verification of this useful approach and methodology for assessing the validity of experimental and computational results. These results are important for further investigations to determine particulate formation mechanisms, to develop combustion models of pollutant formation and to identify fuel additives to reduce particulate formation.

EXPERIMENTAL APPARATUS

Well-Stirred Reactor

A toroidal-shaped WSR research combustor with a volume of 250 mL was used for the study. A cross section of the reactor and jet ring is shown in Figure 2. The design is a modification of an earlier WSR design by Nenniger[1] and Zelina[2] and features an Inconel jet ring with 48 fuel/air jets. The upper and lower halves of the toroidal reactor are cast from silicon carbide. Silicon carbide was used because of its resistance to thermal cracking. The ceramic reactor is contained inside a steel housing, and has a 2-inch diameter stack connected to the exhaust port which forms the plug flow reactor (PFR) section. The jet ring is cooled by nitrogen impingement cooling to avoid autoignition of the fuel-air mixture within the jet ring manifold.

The two fuels used in the current study were neat ethylene and an ethylene-ethanol mixture with 5% of the fuel mass from the oxygen in the ethanol (14.4% ethanol by mass). With these fuels the WSR operates stably at high equivalence ratios ($1.8 < \phi < 2.6$), which allows measurement of PAH, particulates and smoke in a range of conditions from soot inception through the formation of carbonaceous soot.
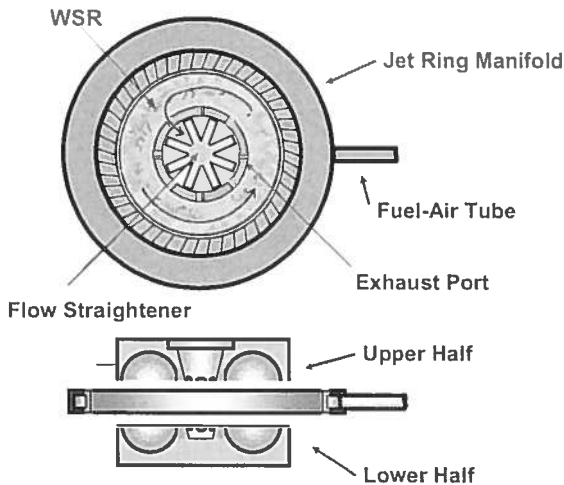
Figure 2: Schematic of WSR Design

Figure 3 is a photograph of the WSR rig during operation which also shows a sampling probe penetrating the exhaust stack, entering the plug flow region above the reactor. Gaseous emissions and smoke were drawn from the PFR section. A port at the bottom of the housing permits probe access to the reactor for obtaining emissions and smoke samples.
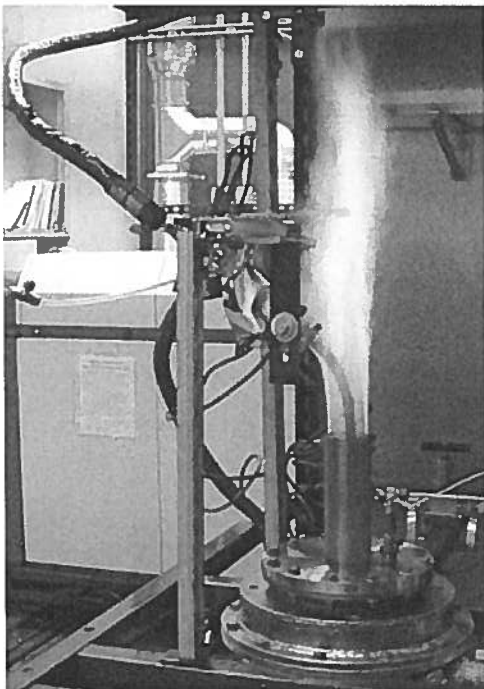

Figure 3: WSR Test Rig Burning Ethylene

Experimental Sampling Techniques

Soot samples were collected on filters from both the plug flow region 16 cm downstream of the WSR and from the inside of the toroidal WSR volume on paper or quartz filters by drawing the exhaust gas collected in the probe through the filters. The gas sample was first pulled through a 25 cm-long oil-cooled probe with an inside diameter of 0.47 cm. The probe was cooled to 150°C by circulating oil through the outer jacket. The gas then passed through an electrically heated (constant surface temperature of 150°C) 2-meter long sample line before passing into a Roseco engine smoke emissions sampler.

The volume of the sample gas collected for each test was 7.08 liters. Each sample required 30-60 seconds to collect. The samples acquired on the paper filters (Whatman #4) were analyzed using the SAE ARP1179 procedure[7] to determine the smoke number based on reflected light from the samples:

$$SN = 100\left(1 - \frac{R_s}{R_W}\right)$$

where: R_s = Reflectance of the stained filter
          R_w = Reflectance of the unstained filter

The samples acquired on the quartz filters (Whatman type-QMA) were analyzed to determine carbon burn-off in a LECO carbon analyzer. The total carbon analyzer measures the carbon mass deposited on the filter by measuring the CO_2 produced while increasing the temperature of the filter in an oven in the presence of excess oxygen. An advantage of the carbon analyzer is that any inorganic deposits on the filter, caused by erosion of the reactor materials will be ignored in the analysis.

In addition to the carbon burn-off analysis, the quartz filter samples were also analyzed using gas chromatograph/mass spectrometry (GC/MS) Chromatoprobe[8] (Figure 4) analysis to determine the PAH content of the soot. This was performed by placing a 2-mg sample cut from the soot stained quartz filter into the sample vial inside the Chromatoprobe shown in Figure 5. The Chromatoprobe was then inserted into the temperature programmable injector (Figure 6) of the GC/MS, which was rapidly ramped in temperature (150°C/min) from 40 to 320°C. This resulted in the PAH's being thermally desorbed from the quartz filter paper and sequentially injected into the GC/MS for separation and detection.
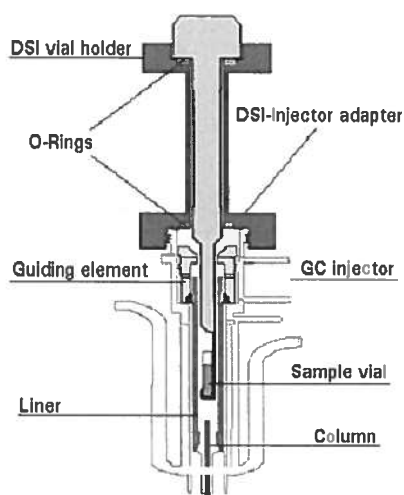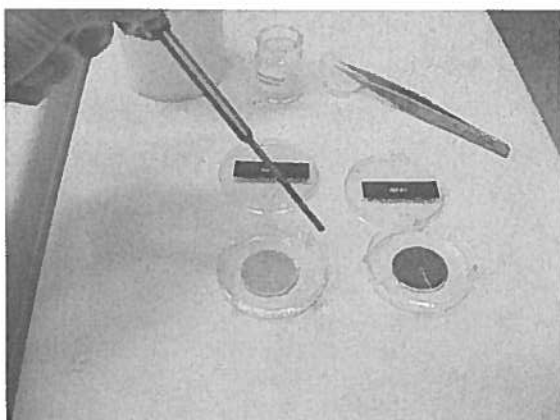
Figure 4: Varian Chromatoprobe

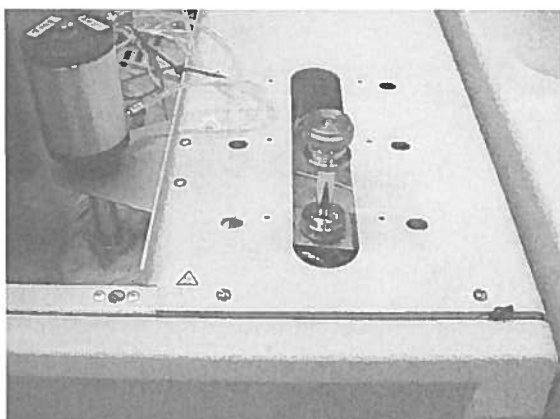**Figure 5: Chromatoprobe Sample**

Figure 6: Chromatoprobe in GC/MS

Seventeen different PAH's identified during the Chromatoprobe analysis are listed in Table 1. Also listed are the target ions for each PAH, which are the most abundant ions from the mass spectrum of each PAH used for detection, along with the retention time, which is the time that the PAH is retained on the GC column before detected by the mass spectrometer. The retention time can be used to distinguish between PAH's with the same target ion.

Table 1. PAH Species Identified in the GC/MS Chromatoprobe Analysis

PAH	Target Ion (m/z)	Retention Time (min)
Naphthalene	128	5.367
Acenaphthylene	152	8.191
Acenaphthene	153	8.460
Fluorene	166	9.262
Phenanthrene	178	10.733
Anthracene	178	10.811
1,4-Diphenylbutadiyne	202	12.350
Fluoranthene	202	12.600
Pyrene	202	12.921
Benz [a] anthracene	228	14.899
Chrysene	228	14.951
Benzo [b] fluoranthene	252	16.809
Benzo [k] fluoranthene	252	16.846
Benzo [a] pyrene	252	17.344
Indeno [1,2,3-cd] pyrene	276	19.237
Dibenz [a,h] anthracene	278	19.653
Benzo [g,h,i] perylene	276	19.817

Emissions from the reactor section of the WSR were passed through a quartz filter to remove particulates and then trapped in a 250-mL gas sampling bulb. Gas samples were directly injected into the GC/MS for qualitative and quantitative analysis of combustion gas species. Seven trace combustion gas species were targeted for analysis and are shown in Table 2 along with their corresponding target ions and retention times.

4

Table 2. Combustion Gas Species Considered in the GC/MS Gas Analysis

Gas Species	Target Ion (m/z)	Retention Time (min)
1,3-Cyclopentadiene	66	0.400
Benzene	78	0.604
Toluene	91	1.094
Ethylbenzene	91	2.164
Phenylacetylene	102	2.485
Styrene	104	2.769
Naphthalene	128	7.980

Particulate and Emissions Measurement Instrumentation

The particulate instrumentation system is composed of a TSI 3022 condensation nuclei counter (CNC) and a sampling system using a vacuum pump to control sample flow through a 10 L/min flow meter and transmitter. This combination of Brooks flow meters is used to set accurate dilution air flows to the particulate sampling probe. The CNC and sampling system are configured to adapt to the PMCMS, shown in Figure 7, used to evaluate particulate species and PAH.
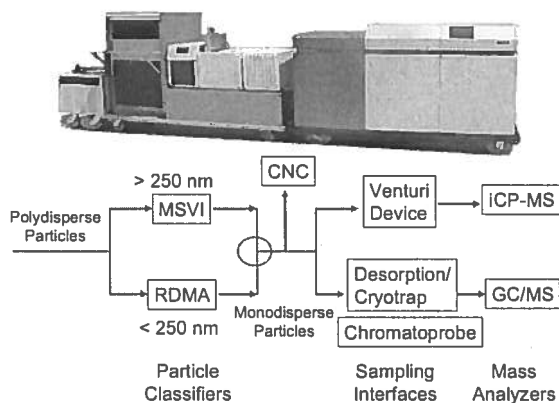

Figure 7: PMCMS and Schematic

Particle size below 250 nm was characterized using the Radial Differential Mobility Analyzer (RDMA)[9] within the PMCMS, shown in Figure 8.
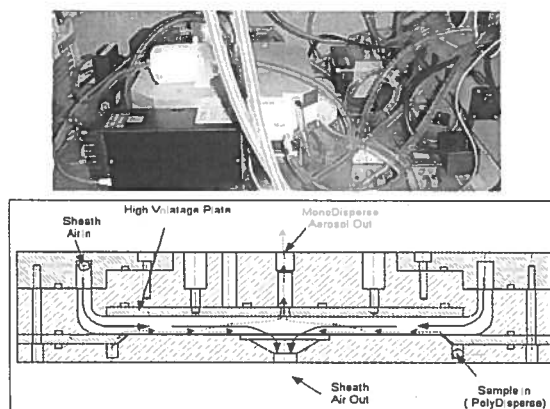

Figure 8: RDMA

Particle sizing is achieved by charging a polydisperse stream of aerosols and passing the stream through a well defined electric field. Charged particles within the aerosol will follow predetermined trajectories. The RDMA is designed to extract aerosols that follow one predetermined trajectory, while discarding all others. The particle number density was determined using the CNC sampling from the PFR in the WSR. A short stack configuration was used to minimize the PFR region for obtaining particulate, smoke and soot measurements close to the reactor. The sample from the PFR was extracted from a region 7 cm upstream of the PFR exit to capture the rich exhaust products before they could react with the ambient air.

The emissions system consists of a 150°C oil-cooled emissions probe and a 150°C heated sampling line that is 6.1 m long. The sample stream is then split into two streams. The first stream directly enters a flame ionization detector total hydrocarbon analyzer, while the second stream enters an Alpha Laval chiller, which provides the main sampling pump, condenses water vapor from the gas sample and sets the sample flow for the CO, CO_2, O_2 and NO_x analyzers. The analyzers are calibrated before each test using 2% certified standard gases and often spanned for verification of ~3% accuracy during the tests, using several calibration gas mixtures to check drift and maintain linearity.

TEST CONDITIONS

The air flow for the experiments was set at a constant 240 g/min with an inlet temperature set at 392 +/- 5K. The fuel/air equivalence ratio, ϕ, ranged from 1.9 to 2.6 for both fuels. The pressure inside the reactor section ranged from 1.1 to 1.7 kPa above the

ambient pressure for all of the experiments. The average residence time in the reactor, τ, which was calculated using: $\tau = \rho V / (m_a + m_f)$, was 9.7 +/- 0.3 ms for the experiment.

The gas temperature inside the reactor (uncorrected for the effects of radiation) ranged from 1480 to 1725 K. The temperatures are significantly lower than the adiabatic flame temperatures because of heat loss through the high-conductivity silicon carbide reactor walls to the nitrogen flow that is used to cool the jet ring.

EXPERIMENTAL RESULTS

The particle size distributions sampled from the plug flow region of the reactor are shown in Figure 9 for both the neat ethylene and the ethylene-ethanol mixtures over a range of ϕ from 2.0 to 2.6. The ethylene-ethanol mixture was shown to reduce particle concentration at all ϕ compared to the neat ethylene fuel. The highest particle concentrations for ethylene and the ethylene-ethanol were measured at $\phi = 2.4$ and $\phi = 2.3$, respectively.
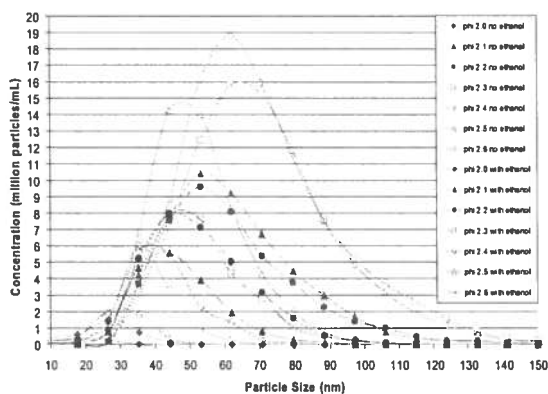
Figure 9: Particle Size Distribution

The diameter of the peak particle concentration for the size distributions is shown in Figure 10. The peak particle size increases as ϕ is increased from 1.9 to 2.3 for both fuels. As ϕ is further increased the peak particle size decreases. The ethylene-ethanol fuel resulted in smaller peak particle sizes compared to the ethylene fuel over the entire range of test conditions.
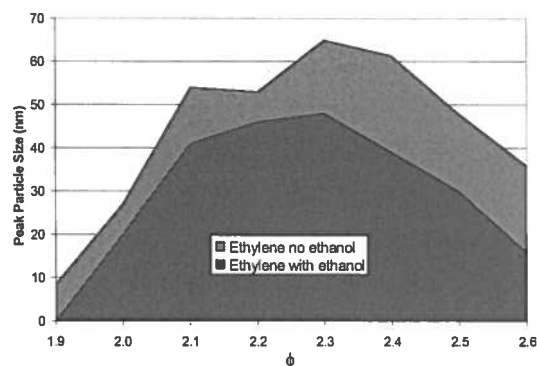
Figure 10: Peak Particle Size

The total particle concentration was calculated by integrating the area under the particle distribution curves for each ϕ, shown in Figure 11. The addition of ethanol resulted in a reduction in the total particle concentration measured over the entire range of ϕ tested. The bottom half of Figure 11 shows the stained quartz filters after the samples were acquired for both the neat ethylene fuel (top row) and ethylene-ethanol mixtures (bottom row) in order of increasing ϕ from left to right. The filter stains for both fuels are darker as ϕ is increased from 1.9 to 2.2 and then lightens as ϕ is further increased. For all ϕ the stains are darker for the ethylene fuel than they are for the ethylene-ethanol fuel.
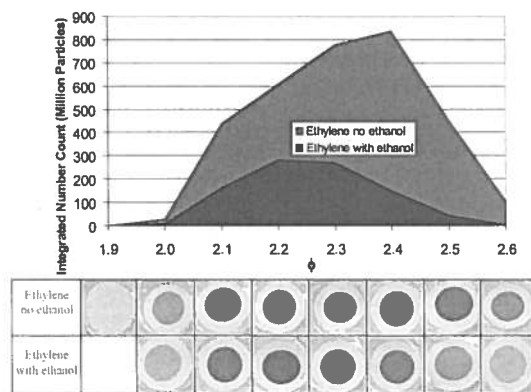
Figure 11: Total Particle Count (Top) and Corresponding Images of Filters from the Plug Flow Region (Bottom)

The GC/MS chromatogram resulting from direct injection of 500 µL of gas sampled from the WSR for a typical test is shown in Figure 12. Benzene was the most concentrated gaseous species detected followed by 1,3-cyclopentadiene and a series of other soot

precursors, whose structures are shown in the figure. These results were similar to those found by Lam et al.[10], where benzene was measured in highest concentration, followed by phenylacetylene, naphthalene, toluene and styrene. The mass chromatogram was magnified 100 times from 10.0-14.0 minutes to show the presence of trace PAH's in this range.
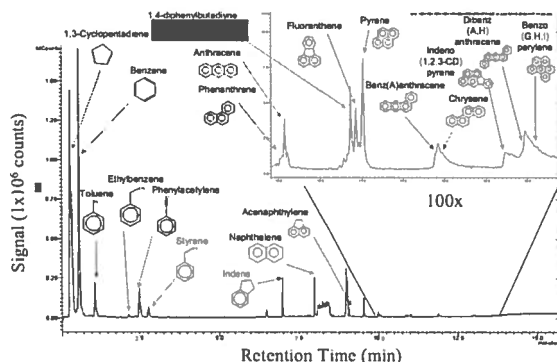

Figure 12: GC/MS Gas Analysis from WSR

A calibration curve was prepared for benzene by injecting 500 µL aliquots of benzene vapor at varying concentrations from a static dilution bottle. The mass of benzene per 500 µL sampled from the WSR is plotted for each ϕ, shown in Figure 13. The concentration of benzene increases linearly with increasing ϕ. The addition of ethanol resulted in no change in benzene content. All other gaseous soot precursors detected indicated a similar trend as benzene.
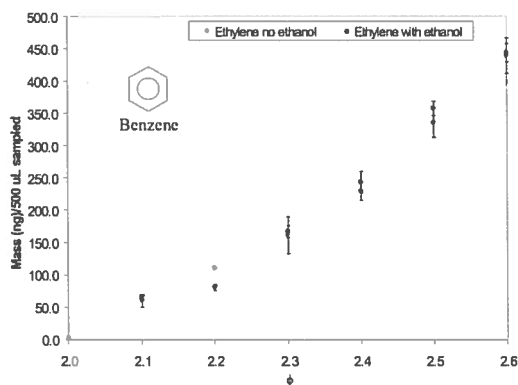

Figure 13: Benzene Concentration Sampled from the WSR

Figure 14 shows the smoke number measured from filter samples extracted from both the reactor and the plug flow section. For both fuels, the smoke number initially increases between ϕ = 1.9 and 2.2-2.3, and starts to decrease as ϕ is increased further. Although there is more fuel available for the formation of soot at higher ϕ, it is thought that the soot production is reduced due to decreasing temperatures and thus slower chemical reaction times. Note that the smoke number measured in both the reactor section and the plug flow regions are approximately equal for the same fuel at the same reactor conditions for ϕ < 2.4. As the fuel flow is further increased, the smoke number is seen to be lower in the reactor section than it is in the PFR.

The addition of ethanol results in a reduced smoke number for all ϕ measured, with the greatest reduction shown at ϕ = 2.2 and 2.3. This trend is different from the one observed previously in the study by Stouffer et al.[5] where the addition of ethanol was seen to slightly increase the soot production. However, it should be noted that the temperature inside the reactor in the previous study was higher (by approximately 110°C) than the reactor temperature in the current study because lower thermal conductivity ceramics were used for the wall materials in the previous study. It is thought that the combustion temperatures significantly affect the soot production mechanism.
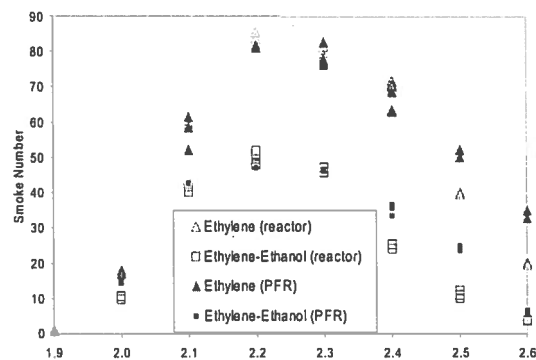

Figure 14: Smoke Number Results

Figure 15 shows total carbon analysis of the quartz filter samples extracted from both the reactor section and the plug flow sections of the WSR. The overall shape of the integrated carbon mass plot shown in Figure 15 shows trends similar to those shown for the smoke number plots in Figure 14. A significant difference is that there was an increase in the total carbon mass between the reactor and the plug flow section. The addition of ethanol decreases the

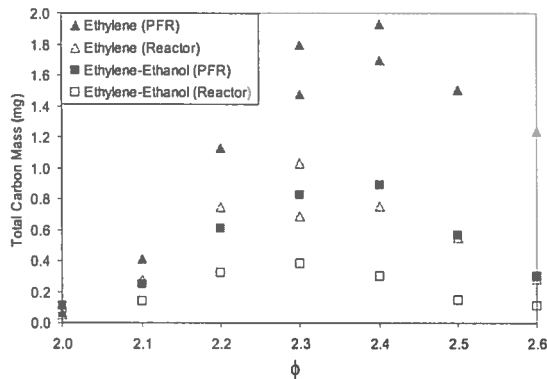amount of carbon deposited on the quartz filters for all φ measured.

Figure 15: Total Carbon Mass

The relative carbon count plotted with increasing temperature for three equivalence ratios (φ = 2.1, φ = 2.3, and φ = 2.6) are shown in Figures 16A, 16B, and 16C, respectively, along with corresponding photographs of the filters before the carbon analysis was conducted. These figures show two distinct peaks, a low temperature peak located between 120 and 160°C, and a high temperature peak located between 450 and 560°C. The sample for the highest equivalence ratio (φ = 2.6 in Figure 16C) has the highest carbon content in the low temperature region and the filter stain is beige-colored while the high temperature carbon peak is highest for the φ = 2.3 case, shown in Figure 16B, which shows a much darker filter stain. It is thought that the low temperature peak is due to the presence of PAH's while the high temperature peak is due to the presence of carbonaceous soot.
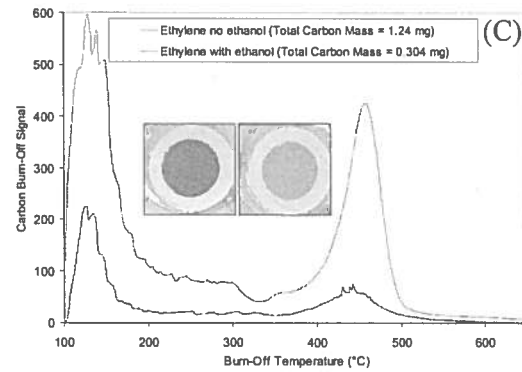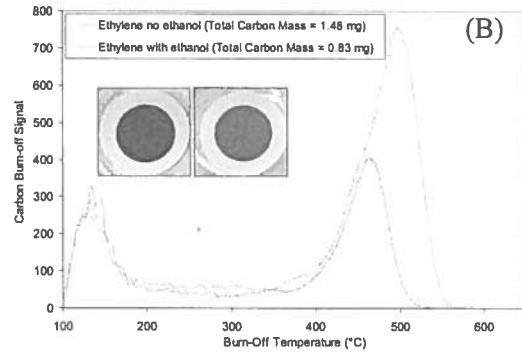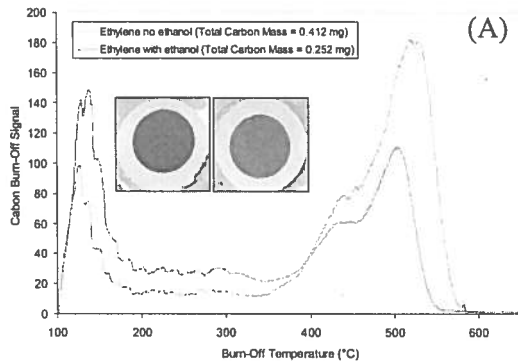

Figure 16: Carbon Vs. Filter Temperature, A (φ = 2.1), B (φ = 2.3), and C (φ = 2.6)

The chromatogram in Figure 17 was obtained from the GC/MS Chromatoprobe analysis of the particulate matter deposited on the quartz filters. Pyrene which is a known soot precursor was shown to be the most concentrated PAH detected and correlates well with total PAH content. Similar results were found by Lam et al.[10], where they saw large concentrations of acenaphthene, pyrene, and phenanthrene in the WSR plug-flow section.
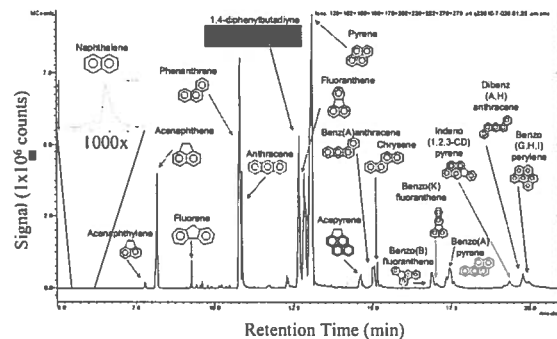

Figure 17: GC/MS Chromatogram of Species Thermally-Desorbed from Filter Samples

Pyrene concentration was determined from Chromatoprobe GC/MS analysis of quartz filters sampled at equivalence ratios (ϕ = 2.0 to 2.6). The concentration curve, Figure 18, follows a similar trend as the curve for total particle counts in Figure 11, indicating a relationship between pyrene and soot production - worthy of further examination. The addition of ethanol reduces the amount of pyrene deposited on the filters for ϕ > 2.2.
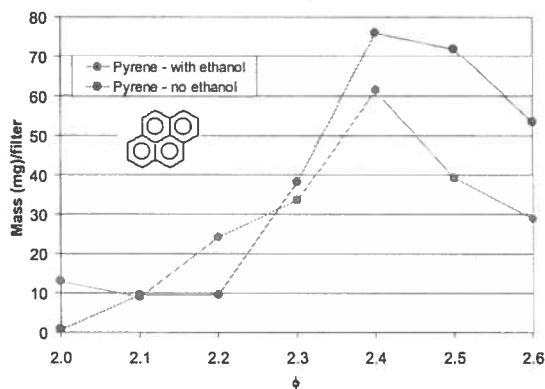

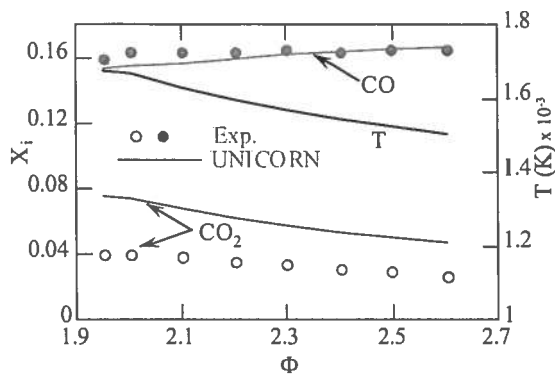**Figure 18: Pyrene Concentration**

MODELING OF WSR FLOW

A time-dependent, axisymmetric mathematical model known as UNICORN[6,11] is developed to simulate the PAH's growth in unsteady flames. It solves for u- and v-momentum equations, continuity, and enthalpy- and species-conservation equations on a staggered-grid system. A detailed chemical-kinetics model of Wang and Frenklach[12] is incorporated in UNICORN for the investigation of PAH formation in acetylene and ethylene flames. It consists of 99 species and 1066 elementary-reaction steps. Thermophysical properties such as enthalpy, viscosity, thermal conductivity, and binary molecular diffusion of all the species are calculated from the polynomial curve fits developed for the temperature range 300 – 5000 K. Molecular diffusion is assumed to be of the binary-diffusion type, and the diffusion velocity of a species is calculated using Fick's law and the effective-diffusion coefficient of that species in the mixture. A simple radiation model based on optically thin-media assumption was incorporated into the energy equation. Only radiation from CH_4, CO, CO_2, and H_2O was considered in the present study[13].

The finite-difference forms of the momentum equations are obtained using an implicit QUICKEST scheme, and those of the species and energy equations are obtained using a hybrid scheme of upwind and central differencing[11]. At every time-step, the pressure field is accurately calculated by solving all the pressure Poisson equations simultaneously and utilizing the LU (Lower and Upper diagonal) matrix-decomposition technique.

The WSR flow was modeled by assuming it as uniformly (in cross section) reacting gas flowing through a tube having a diameter and length of 51 and 150 mm, respectively. The formation of flame in the swirl section is highly three-dimensional and is not modeled in the present study, even though, it is believed to have significant influence on the generation of certain PAH species. These assumptions forced the model to make use of the prescribed temperature profile as input condition. The temperature distribution for each case along the length of the straight section of the WSR is constructed from the measurements made in the swirl section. A temperature drop of 100 K was assumed between the swirl and probe (150 mm) locations. Steady state calculations are performed for each case and the results are compared with the measurements in Figure 19.

The model predicts the CO concentration well, and over predicts the concentrations of stable species such as CO_2 (Figure 19A). As the model proved to predict CO_2 reasonably well in other systems such as burner-stabilized flames[14], the discrepancy noted in the present work could be attributed to the assumptions made in for the WSR flow. A good comparison between the predictions and measurements is obtained for benzene and acenaphthylene (Figure 19B). Note, samples of benzene were extracted from the reactor in gas phase while that of acenaphthylene were obtained in solid phase. On the other hand, the model seems to under predict the concentrations of heavier PAH species (Figure 19C). It is known that the inception of PAH species starts in the low temperature (~1200 K) region on the fuel side. Since the present model for WSR completely ignores the flame formation in the swirl section, prediction of lower amounts of PAH's should be expected.
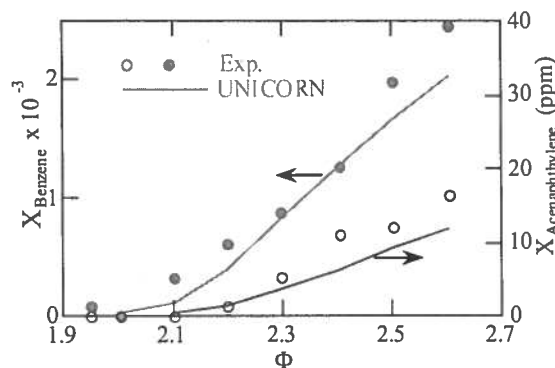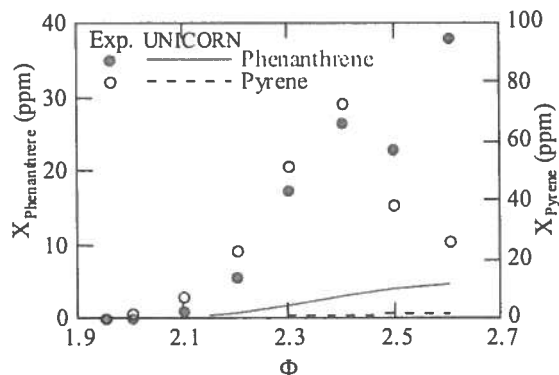
Figure 19: Predicted and Measured Species concentrations for Ethylene-Air Mixtures (A) Major species, (B) Benzene and Acenaphthylene, (C) Phenanthrene and Pyrene.

SUMMARY AND CONCLUSIONS

Experimental results from fuel-rich ethylene-air and ethylene-ethanol-air mixtures, where ethanol (5% of mixture) was used as a particulate reducing additive, were obtained using a WSR research combustor.

It was found that:

1. The PMCMS is capable of measuring particle size, particle distribution, and detailed chemical analysis of combustion products.
2. Particle count was reduced by 60% and peak particle size was reduced by 30% with ethanol addition to ethylene-air mixtures.
3. Large concentrations of benzene were found in the WSR, which increased linearly with increasing equivalence ratio. The benzene concentration was independent of additive addition.
4. A maximum 40% decrease in smoke number was observed with ethanol addition, with the maximum reduction occuring at $2.3 < \phi < 2.6$.
5. Carbon analysis of filter samples indicated two distinct carbon burn-off peaks attributed to PAH and carbonaceous soot deposits. These peaks shift in magnitude and temperature depending on the stoichiometry.
6. Pyrene was found to be a major PAH species, which correlates well with soot production.
7. These results suggest that pyrene, benzene and other PAH's can be used to predict soot formation in modeling and simulation routines for more complex practical combustion systems.

FUTURE RESEARCH PLANS

The WSR has been modified with the capability to vaporize heavier-hydrocarbon fuels such as heptane, toluene and JP-8 jet fuel. These pure compounds and practical fuels will be tested with various fuel additives to investigate soot mitigation processes. Long-term plans include the ability to predict soot formation in practical combustion systems by using detailed chemistry of soot precursors and the analysis of particle chemical content as a function of particle size.

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